

## MEASUREMENT OF ORGANIC SULFUR IN FOSSIL FUELS

K.C. Hsieh, B.T. Tseng, M. Buckentin and C.A. Wert  
Materials Research Laboratory and Department of Metallurgy and Mining  
Engineering, University of Illinois, Urbana, IL 61801  
and

Gary Dyrkacz  
Chemistry Division, Argonne National Laboratory  
Argonne, IL 60439

### ABSTRACT

A method of direct determination of the organic sulfur content of solid fossil fuels has been developed using the transmission electron microscope. The technique uses the detection of the  $K\alpha$  line of sulfur to measure the presence of sulfur and the volume from which this radiation comes is measured using the bremsstrahlung radiation counted simultaneously with the sulfur line. Applications have been made to the organic sulfur content of whole and treated coals, to amber and to kerogen in oil shale. The greatest value of the method is its ability to measure the variation of organic sulfur content over extremely fine distances.

### INTRODUCTION

Sulfur is found in coal in two principal forms: mineral sulfur (principally pyrites) and organic sulfur distributed through the carbonaceous matter. The conventional method of determination of the organic sulfur content is a two step process (1). First, total sulfur is measured. Then the pyritic and sulfatic sulfur is determined after selective dissolution of the minerals with acids. The organic sulfur is calculated as the difference between the total sulfur and the mineral sulfur. This commonly used ASTM procedure (method D 2492) is apparently sound when applied to raw coals, but there may be problems with analysis of chemically processed coals (2,3). Furthermore, this method provides only an average sulfur concentration and is unable to distinguish among possible variations either spatially or among the maceral types.

A number of investigators have examined the possibility of direct measurement of organic sulfur in coal which does not depend upon this difference technique. These methods have commonly utilized the x-ray emission lines of sulfur to detect its presence and have used a variety of standardization techniques to provide numerical data and to differentiate among the variety of sulfur forms which may be present. Several earlier papers have described these techniques (4-11). Among them, the extensive work of Raymond and Gooley and of Straszhheim and Greer should be especially noted. The resolution of these techniques using either the electron microprobe or the SEM is about  $5\mu$ , so the volume of each measurement is immensely less than that of the standard ASTM technique. Determination of average values using the microprobe or SEM instruments does require the averaging over a number of individual observations to take account of possibility of variability in organic sulfur content from place to place in the coal.

We have extended this electron-optical technique to even finer spatial resolution using the transmission electron microscope. The specimens are either finely divided powders or foils of coal which are thin enough to be practically transparent to the electron beam. The technique has been adapted from methods developed by Hall and his collaborators for measurement of organically dispersed elements in biological tissue (12-15). We have developed applications of the technique, standardized the method for our microscope and have presented first results in a publication in Fuel (16). We refer only briefly to the chief features of the technique here.

## THE TEM METHOD

The geometry of the measurement is sketched in Fig. 1. An electron beam is incident upon a coal foil which is less than  $1\ \mu$  thick. Ionizing collisions with atoms in the irradiated volume cause the emission of characteristic x-ray lines which can be counted by an appropriate detector. At the same time, the background radiation is counted from the same volume. The  $K\alpha$  line of sulfur has an energy of about 2300 eV and we measure the bremsstrahlung radiation over the range 10-18 keV; a typical spectrum is sketched in Fig. 2. The organic sulfur concentration of the volume being irradiated by the electrons is simply related to the ratio of these two count rates:

$$S(\text{wt}\%) = A C_S / C_b \quad 1)$$

We have found this equation to be well satisfied for thin specimens and have determined the proportionality constant A using known sulfur standards. For our instrument and the geometry of our detector, A has the value 1.6. This number varies slightly among the coals because the bremsstrahlung radiation is somewhat dependent on the C/O ratio in the hydrocarbon matrix. This variation is slight however, being only a few percent for coals from the sub-bituminous to anthracite range.

We emphasize that success of the method is achieved only if the coal foil is thin enough that the electron beam is essentially undiminished in passing through the foil so that the intensity of ionization of the elements in the coal is uniform throughout the irradiated volume. Furthermore no absorption of either the sulfur line or the bremsstrahlung radiation should occur in the specimen. For coal foils less than  $1\ \mu$  in thickness, these conditions are amply met.

## APPLICATIONS TO COAL

### Measurement of the Average Organic Sulfur Content

We have tested the technique using a high organic sulfur bituminous coal and a low organic sulfur anthracite. Ten thin foils from each coal were prepared and five measurements were made on each foil. The total of fifty measurements for each coal is averaged to give the organic sulfur content. The organic sulfur content of a third coal, a low sulfur bituminous, was determined by examining the sulfur content of powdered macerals. The graph in Fig. 3 shows that results from this method compare very well with those from the standard ASTM method for these three coals. We could make additional measurements of this type, but we have elected to utilize the most valuable feature of this technique, namely the spatial variation.

### Spatial Variation of the Organic Sulfur Content

A measurement was made over a coal maceral (presumably vitrinite) in an Illinois #5 coal. That variation is sketched in Fig. 4. The average value is about 2.6 wt% organic sulfur with a variation of about 25% about this mean. At one point in the maceral a slight excursion away from the edge showed a much higher organic sulfur content locally, some 3.5%.

We have made additional measurements of variation of sulfur concentration around mineral particles in coal, and find some variation. We were not completely sure that that variation was not a function of the maceral type in which the mineral was located, rather than being due to the mere presence of a mineral. Consequently, we need to carry out additional work to show the factors on which this variation depends. In particular, we are interested to see whether the organic sulfur varies as one approaches closely to a sulfide particle or whether it remains constant right up to the edge of the particle. Further, we would like to see whether the organic sulfur concentration in the vicinity of a sulfide is

altered as the coal is heated into the temperature range where sulfides are known to decompose (some 700 K). Measurements of both types are in progress.

#### Variation of Organic Sulfur Between Submaceral Types

We wished to see whether the variation we observed in organic sulfur content in repeated measurements on some coals was due to random spatial variation or whether it might be due to variation in sulfur content of maceral types. It is known that the organic sulfur content of coals varies in the order  $S(\text{exinite}) > S(\text{vitrinite}) > S(\text{inertinite})$ . Our technique seems to have the capability of determining this on a fine scale. We have made measurements on a coal which had been separated into maceral fractions. We used an Indiana bituminous coal, PSOC 106, which had been separated into maceral fractions by the gradient-centrifuge method employed at the Argonne National Laboratory (17,18). Our first measurements on the gross maceral types showed the expected general trend. For the inertinite the average was 0.428 wt%, for the vitrinite, 0.61 wt% and for the exinite 1.2 wt%. Multiplying these numbers by the known fractions of the maceral types gave an average value of 0.64 wt% S, observations made by Dyrkacz independently gave an average value of 0.57 wt%. His measurements are discussed further in more detail (19).

The most significant feature of these measurements was not the average values, but the range of organic sulfur content for the three maceral types. In particular, the exinites gave wide variation, from 0.03 to 2.31 wt% for the fifty-five observations made on that maceral type.

We then took maceral fractions separated on an even finer scale so that the organic sulfur content of submaceral types could be determined independently of each other. We took 12 density fractions of this coal, 5 exinites, 3 vitrinites and 4 inertinites. Each was measured independently. Data for these three vitrinites are displayed in Fig. 5. These graphs show the organic sulfur content measured over many micron size particles of particular density fractions. The averages are listed on the graphs and the spread about the averages is evident.

A plot of the average organic sulfur content of all 12 maceral fractions is shown in Fig. 6. One sees a gradual curve, rising from the dense inertinites toward the lighter vitrinites into the exinite. Then the curve goes through a high value at a density around 1.18, and falls off toward the lighter fractions.

The peak value of organic sulfur content about the density 1.18 is striking. Since it is believed that the maceral sporinite has about this density, we elected to measure the organic sulfur content of an individual sporinite maceral embedded in whole coal, not separated from its surrounding by fine grinding. A specimen of Illinois #5 coal was examined by reflectance microscopy until a sporinite maceral was observed embedded in surrounding vitrinite macerals. A hole appropriate for electron microscope observation was milled at this point. The organic sulfur content of this area was measured from one vitrinite maceral through the sporinite into the other vitrinite maceral. As was expected, the organic sulfur content of the sporinite maceral was much higher than that of the surrounding vitrinite macerals, see Fig. 7. Furthermore, the organic sulfur content rises sharply at the boundary between the vitrinite and sporinite macerals.

This poses an interesting question. Is the high organic sulfur of sporinite a function of high organic sulfur in the initial spore and would it be true for pollens as well? We are examining these questions.

## AMBER

Amber is a fossilized resin from either deciduous trees or needle trees. It is akin to the resinite maceral type in coal. Therefore we desired to measure the organic sulfur content of amber to see how it would fit in this scheme. A measurement on an amber of Dominican origin showed that the organic sulfur content was low, much less than 1%, and that it varied from about 0.14 to 0.3 with an average value over six measurements of 0.2 wt% sulfur. Similar measurements for a Baltic amber gave an average value of about 0.33% organic sulfur with only a small variation about this mean. These measurements are consistent with the data in Fig. 6 which indicate that resinite, a low density maceral, should be on the lower end of a curve such as that in Fig. 6. We are now examining resinite maceral fractions taken from whole coals to determine the validity of this observation.

Amber also has other lines in the x-ray emission spectrum showing that other elements may be present in organically distributed form, see Fig. 8. In addition to the  $K\alpha$  line of sulfur, lines for Cl, K and Ca are present. We believe that these elements too are organically distributed, although one cannot rule out the possibility of there being tiny precipitates below the limits of resolution of the electron microscope (some 20 Å or so). Since lines for Al, Si and heavy metals are absent, precipitates of a clay-like nature or of minerals containing iron, copper and other heavy metals are not to be seen. The measurement does show that organic elements other than sulfur might be detected and measured using the electron microscope technique, with appropriate standardization of the constant A in Equation 1.

## OIL SHALE

Oil shale contains carbonaceous matter distributed in pores in the massive mineral crystals and also as an interparticle film between the mineral crystals. An electron microscope observation of a thin foil of a Green River shale from the mahogany zone is shown in Fig. 9. The kerogen is the light material between the dark mineral blocks. One also sees that smaller minerals are also embedded within the kerogen film; in this particular specimen they are a phosphate. We have measured the organic sulfur content along a line in a kerogen film over a distance of about 100  $\mu\text{m}$ . Six observations were made; they range in value from 0.2 wt% to 1.3 wt% with an average value over 6 randomly spaced points of about 0.4 wt% sulfur.

We emphasize that this technique is a valuable method of measuring the organic sulfur content of the carbonaceous matter in oil shale in situ. Furthermore, the variation over different regions in the kerogen could readily be determined.

## SUMMARY

The technique we have described measures the organic sulfur content of fuel materials directly. It must be standardized to a particular microscope and detecting system. Small variations in the proportionality constant A exist among the various carbonaceous matrices, but these are at most 5-10%. The technique is probably not valuable for measuring the average organic sulfur content of coals where the standard ASTM method might be employed, since the electron microscope is expensive to use and demands careful specimen preparation. However, it has high potential for measuring the organic sulfur content of kerogen, tar sands and other carbonaceous material in situ. Its greatest value, though, seems to lie in its ability to measure small spatial variations in organic sulfur content and in determining the variation of organic sulfur concentration among maceral types in either whole or treated coals. Finally it has promise in determination of changes in organic sulfur content which accompany heat treatments or chemical treatments.

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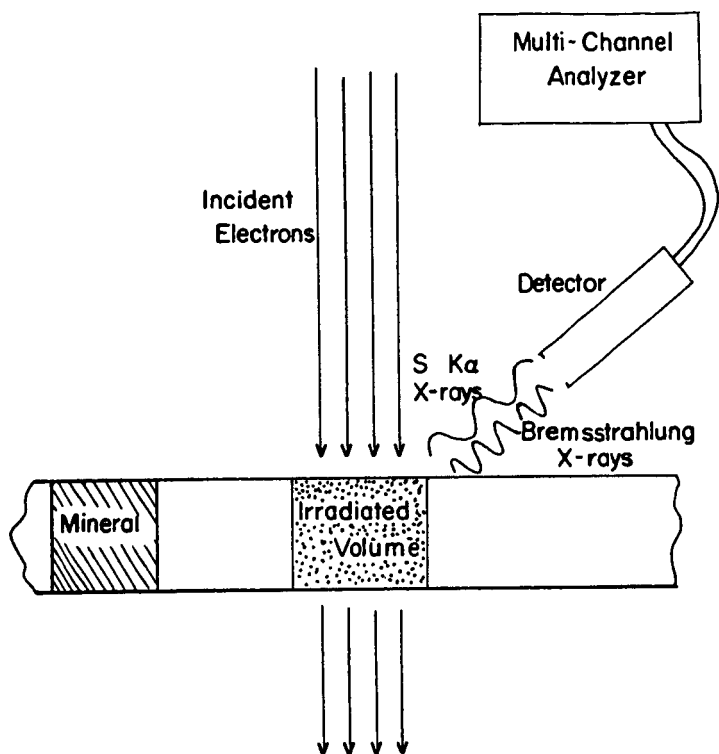


Figure 1. Sketch of x-ray detection system.

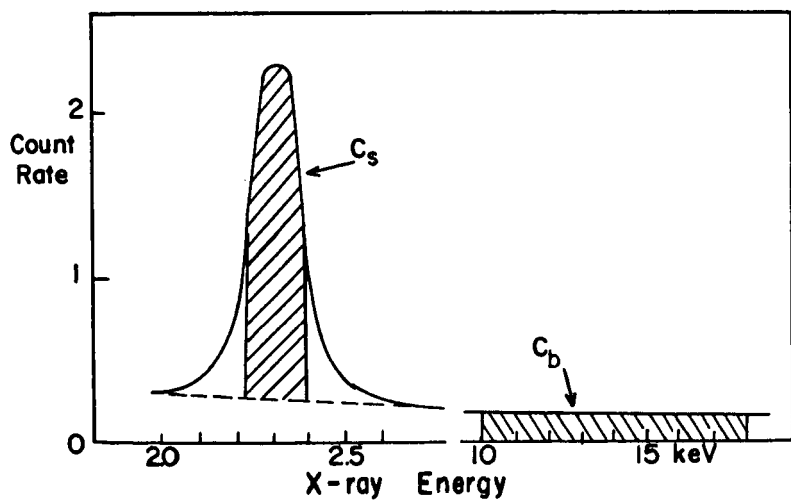


Figure 2. Schematic of counting signals.

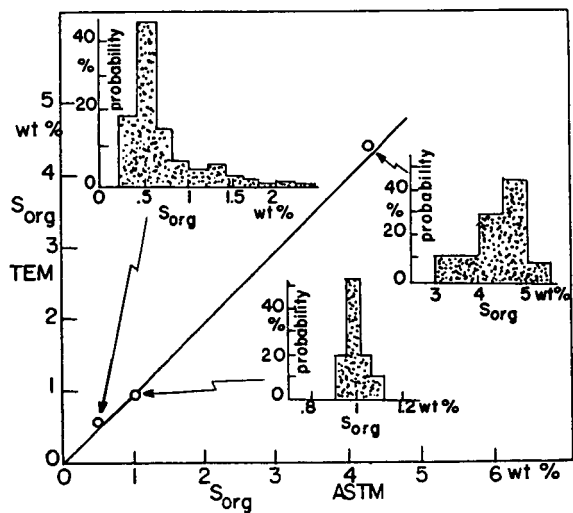


Figure 3. Correlation of measuring techniques.

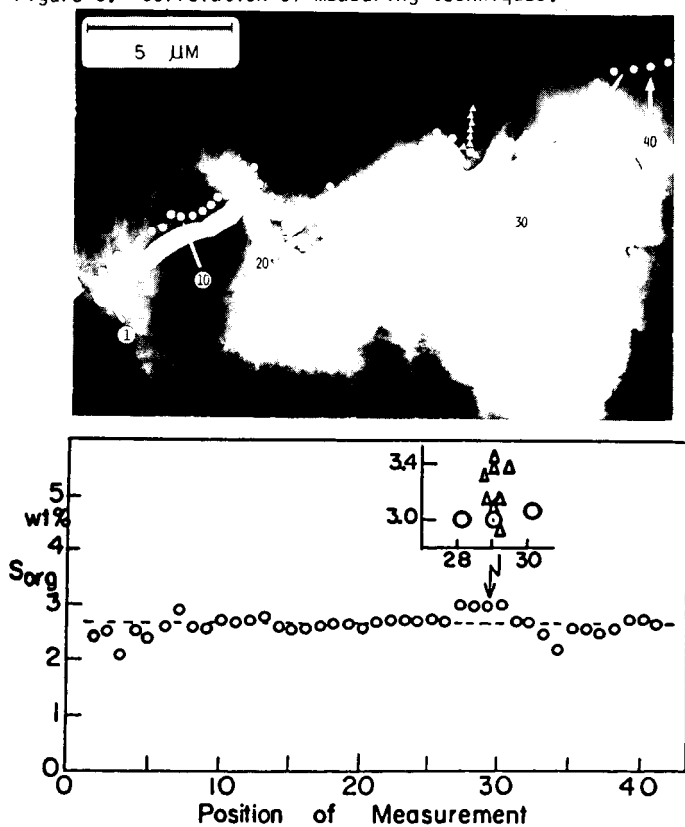


Figure 4. Spatial variation of organic sulfur.

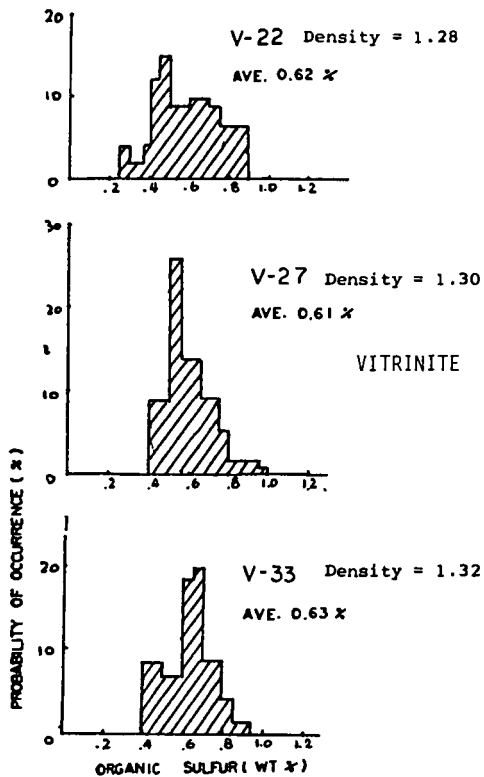


Figure 5. Distribution of  $S_{org}$  concentration.

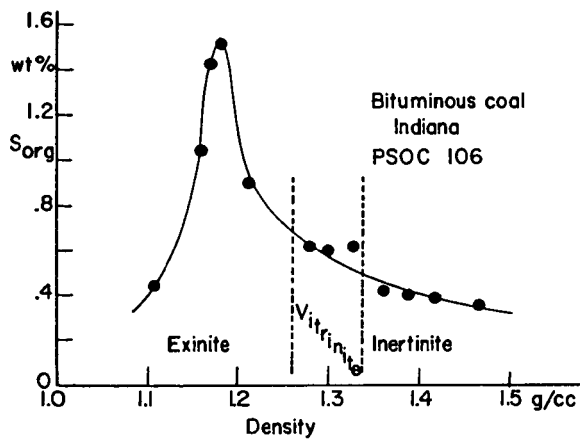


Figure 6. Variation of  $S_{org}$  by maceral type.



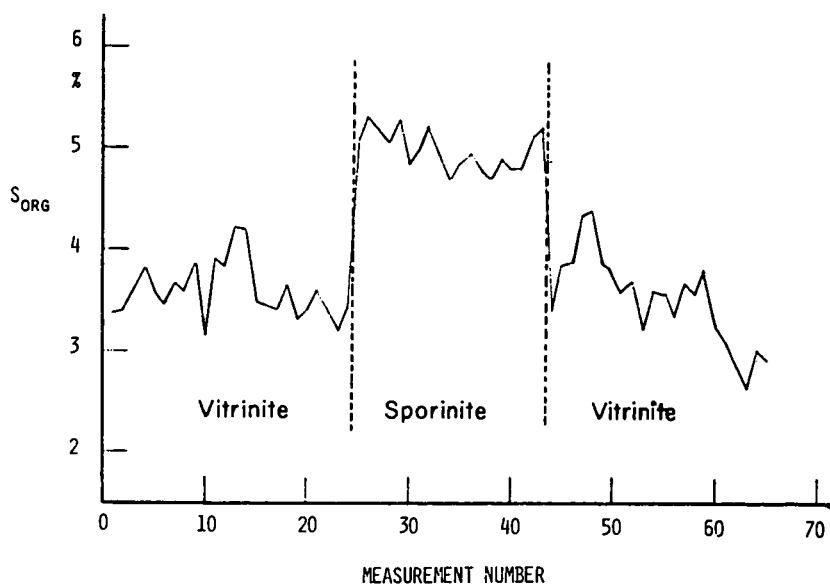
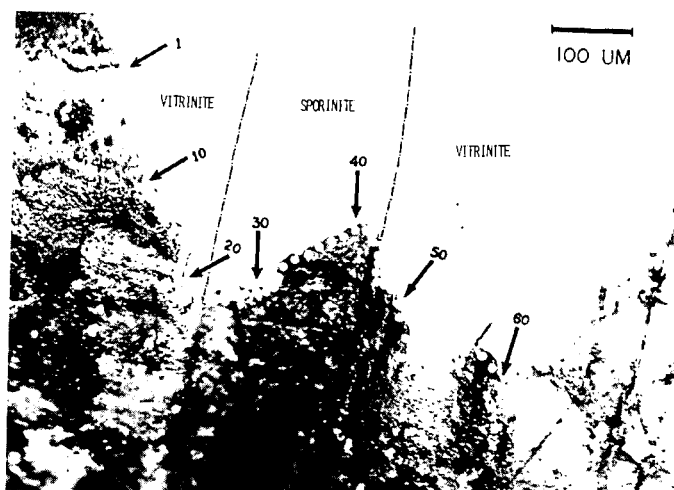


Figure 7. Variation of  $S_{org}$  across a sporinite maceral.

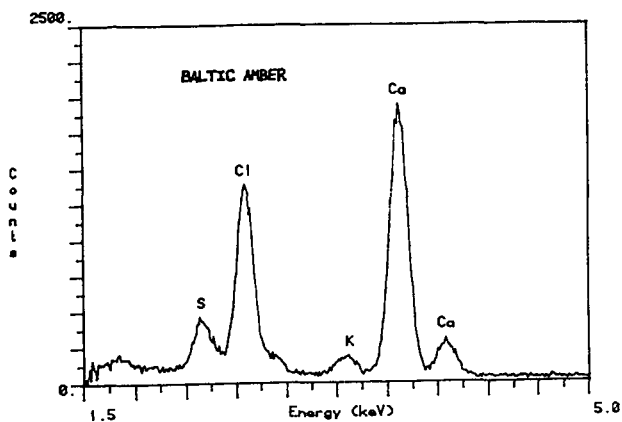


Figure 8. X-ray emission spectrum for amber.



Figure 9. Electron micrograph of oil shale.